INVESTIGATION OF "BITTERNS" AS A SOURCE FOR HEAVY WATER

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1. Introduction

Heavy water of almost 100 per cent. purity has become an important material as moderator-coolant for nuclear reactors. Its occurrence in natural waters is rather low,—0·0145 mol. per cent. being the normal approximate abundance figure,[1]—which is equivalent to one part of Heavy Water in 6,900 parts of natural water. Uptil now no natural source of higher content of heavy water has been made known. Earlier investigations have indicated that practically all the naturally occurring water sources in the world contain heavy water of almost the same average of 0·0140–0·0150 mol. per cent.[2] Somewhat higher content of heavy water was found to occur in the waters of some glaciers, to the extent of an average value of 0·0148,[2] which is a very insignificant increase above the average normal abundance figure, and which may probably be due to still solar evaporation of some part of the ice.

In the course of this observation, it appeared worthwhile to search for such enrichment processes as distillation, adsorption, evaporation, which may go on in nature on a large-scale. Consequently an investigation in the existence of such natural processes was made. In the course of such search for suitable processes, we came across the solar evaporation of sea water, which is going on along with marine salt production on a large scale, and which is a very common process in many parts of the world, where solar heat is available in abundance and where other conditions are suitable, for instance, along the coastal lines of India. This process—it was assumed—should result in some enrichment of heavy water, supposing the degree of evaporation would be sufficiently high to find such enrichment appreciable.

2. Investigation in Natural Enrichment Process

In the more detailed investigation of the nature and the type of this process it was found to be of the type of still evaporation which is going on at rather low temperature, and would, as far as the earlier stages are concerned, conform to a so-called differential distillation at low pressures which is governed by Rayleigh's equation.

In the latter stages of this process, evaporation would take place from more and more concentrated solution, which ultimately becomes almost saturated. The low temperature conditions would establish similarity to [illegible] which is specially suitable for heavy water separation on account of [illegible] coefficient of this separation process at lower [illegible]

Calculations were, then, undertaken to ascertain the evaporation ratio of the solar evaporation process, and it was found that this ratio is of the order of 50 to 70 : 1 parts of water evaporated. This ratio is sufficiently high [illegible] for certain enrichment. Calculations with the help of Rayleigh's equation, using these values, and on the assumptions of most likely temperature prevailing in the solar evaporation process, for instance, 40° C., indicated that enrichment of heavy water from 0·0145 to 0·0224 mol. per cent could be expected in the water remaining in the mother liquor. Then investigations on the D_2O content of the water remaining in the mother liquor of the solar evaporation process, the so-called "Bitterns",[4,6] have been undertaken.

Here, it appears necessary to give a short account of the process of solar salt production.[5] Although, there exist many variations from this procedure, sea water of 3° Bé, or similar sub-soil brine is continually fed to a number of salt pans made from earth which are called the condenser part. In these pans the bulk of water is being evaporated, and the density of brine is gradually brought to about 25° Bé, during which period practically no salt precipitation takes place. However, $CaCO_3$ and Gypsum are almost completely separated out to the extent of which they are present. The brine is then shifted to similar pans, called the crystalliser section in which further concentration to 30° Bé or 32° Bé with simultaneous precipitation of most of the sodium chloride content takes place. Upto 30° Bé of the mother liquor, sodium chloride of approximately 98% purity is obtained while with further concentration to 32° Bé and beyond [illegible] higher quantities of $MgSO_4$ are precipitated and the average NaCl content of the salt is decreased to about 90 per cent. The remaining mother liquor contains mainly $MgCl_2$, $MgSO_4$, NaCl, KCl, and Bromides. It is called "Bitterns", and in most cases, after separation from precipitated salt, it is released back to the sea and lost. In some cases, it is utilised for recovery of Bromine, $MgSO_4$ and KCl. The progress of solar evaporation and change in composition of brine, and subsequent precipitation of salts is represented with data[5] in Table I and graphically in Figs. 1 and 2, and the composition of the Bitterns is [illegible] in Table II.

If the differential progress of the evaporation is being evaluated from available data as we have done in Table I, one can observe, as shown in Figs. 1 and 2 that the specific evaporation of water decreases continually with concentration of the brine and that it becomes enhanced during the precipitation of the common salt (NaCl). This effect of which we did not find any reference so far, is most probably due to release of heat of crystalization, as no increase of volatility of supernatant liquid due to salt precipitation should be expected.

From the shape of the Curve II of Fig. 2, it can be seen that a similar effect occurs already along with the precipitation of $CaCO_3$ and Gypsum.

TABLE I

Concentration and Evaporation Data of Solar Evaporation of Sea water Mediterranean)

(Columns 1 and 2 are taken from the *Report of the Salt Experts Committee*, Government of India, New Delhi, 1950, Page 18).

1	2	3	4	5	6	7	8	9	10
Brine conc. in °Bé at 21° C.	Volume on evaporation in litres	ΔH_2O evaporated in litres	$\Sigma\Delta H_2O$ evaporated in litres	Average $\Sigma\Delta H_2O$ evaporated in litres	Average volume of H_2O evaporated in successive stages in litres	Δ° Bé increase in °Bé within different stages	$\frac{\Delta H_2O}{\Delta ^\circ\text{Bé}}$	$\frac{\Sigma\Delta H_2O}{\Sigma ^\circ\text{Bé}}$	Average Δ °Bé
3·50	100·00								
7·10	53·30	46·70	46·70	23·35	23·35	3·6	13·0	13·0	5·3
11·50	31·60	21·70	68·40	34·20	57·61	4·4	4·94	9·77	9·3
*14·00	24·50	7·10	75·50	37·75	71·95	2·5	2·83	7·18	12·75
*16·75	19·00	5·50	81·00	40·50	78·25	2·75	2·00	6·11	15·375
20·60	14·45	4·55	85·55	42·75	83·275	3·85	1·18	5·00	18·675
22·00	13·10	1·35	86·90	43·45	86·225	1·40	0·965	4·70	21·3
†25·00	11·20	1·90	88·80	44·40	87·85	3·00	0·632	4·13	23·5
†26·25	9·50	1·70	90·50	45·25	89·65	1·25	1·36	3·98	25·625
27·00	6·40	3·10	93·60	46·18	92·05	0·75	4·14	3·99	26·625
28·50	3·90	2·50	96·10	48·05	94·85	1·50	1·667	3·85	27·75
30·20	3·02	0·88	96·98	48·49	96·54	1·70	0·520	3·63	29·35
32·40	2·30	0·72	97·70	48·85	97·34	2·20	0·327	3·38	31·3
35·00	1·62	0·68	98·38	49·19	98·04	2·60	0·261	3·12	33·7

* Precipitation of $CaCO_3$ and $CaSO_4.2H_2O$ starts.

† Precipitation of NaCl starts.

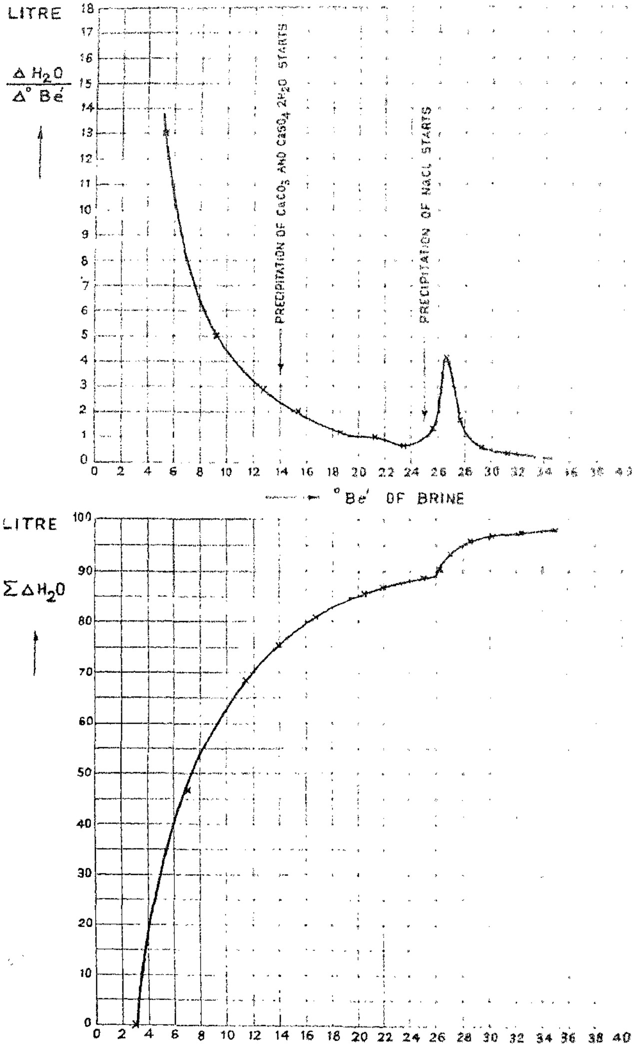

FIGURE 1.

DIFFERENTIAL AND ACCUMULATIVE EVAPORATION OF SEA-WATER DURING THE MARINE SALT PRODUCTION PROCESS.

TABLE II

Composition of Bitterns from Mithapur, India

Density = 29·5° Bé, equivalent to 1·255 specific weight at 25° C.

Constituent	Percentage by weight (of Bitterns)	Percentage by weight (of dry residue)
$NaCl$	7·52	27·4
KCl	1·92	7·0
$MgCl_2$	15·19	55·2
$MgSO_4$	2·80	10·4
TOTAL	27·43	100·0

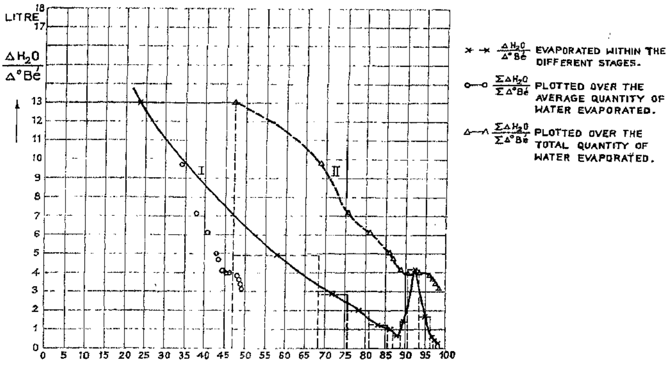

FIGURE 2.

DIFFERENTIAL EVAPORATION OF SEA-WATER DURING THE MARINE SALT PRODUCTION PROCESS.

An example calculation of the evaporation ratio for "Bitterns" of 29·5° Bé gives the value as follows:—

100 litres of sea-water of density 1·027 contains approximately 3·47 kg. fixed residue, and hence 102·7 − 3·47 99·23 kg. of pure water. This 100 litres of sea-water are evaporated approximately to 2 litres of Bitterns of specific weight 1·255 in the marine salt production process. This 2 litres contain 0·69 kg. of fixed residue, and hence, contains 2·51 0·69 1·82 kg. of pure water, including the crystal water in different salts of Bitterns. Evaporation ratio, therefore, is

$$\frac{99\cdot23}{1\cdot82} : 1 \quad 54\cdot5 : 1$$

Therefore, out of 100 litres sea-water 99·23 − 1·82 97·41 kg. water are evaporated by the action of solar heat. For this, 55,600 kcal. are required. The evaporation of the remaining water in the Bitterns will require [illegible] only another 1,140 kcal. Hence about 98 per cent. of heat energy has been supplied by solar energy and consequently invested in the Bitterns.

3. SEPARATION OF WATER FROM SALTS OF BITTERNS

(*a*) *Separation by Crystallization.*—After the first stage of distillation in nature, it was necessary to separate the water part of Bitterns from its composition of different salts. This could be achieved either by distillation or by crystallization. The latter method was only tried tentatively and was not found very suitable for arriving at quick results—as, a temperature below 40° C. is required to precipitate a part of the salt content, and separation was not very effective, as most of the salts crystallized with high crystal-water content, which would have to be separated again.

(*b*) *Separation by Distillation.*—Separation by distillation was found to be more effective which resulted in about 53 per cent. recovery of distilled water from the Bitterns.

With the progress of distillation, more and more salt precipitates out, which interferes with the distillation and has, therefore, to be removed from time to time. Below 124° C., superheating and decomposition of salts could be avoided. However, at higher temperature at latter stages of distillation, decomposition of chlorides takes place due to superheating, and the distillate becomes acidic. After the completion of distillation, still some more water is left in the salt cake as crystal water. To separate crystal water from the salt cake, the latter was dry distilled upto 400° C. in a separate operation, and the highly acidic water was recovered as condensate, and kept separately. Water, thus separated by distillation, was acidic of pH = 3·5, and was further treated as follows:—

The distillate, made alkaline to pH = 8·5 by addition of solid NaOH, was again distilled. This distillation gave pure and neutral distilled water with very little residue. In order to be absolutely safe, the second distillate was again distilled after alkalization and addition of permanganate, and in some cases such distillation was repeated upto 4 or 5 times.

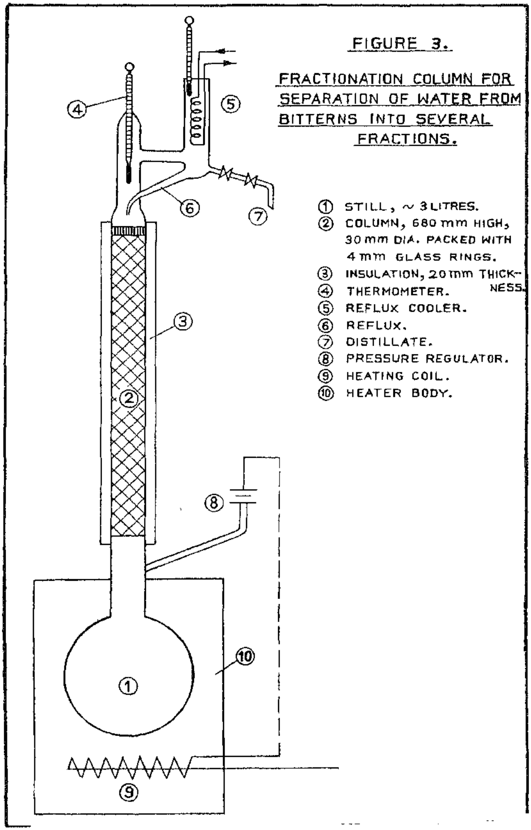

FIGURE 3.

FRACTIONATION COLUMN FOR SEPARATION OF WATER FROM BITTERNS INTO SEVERAL FRACTIONS.

① STILL, ~ 3 LITRES.
② COLUMN, 680 mm HIGH, 30 mm DIA. PACKED WITH 4 mm GLASS RINGS.
③ INSULATION, 20 mm THICKNESS.
④ THERMOMETER.
⑤ REFLUX COOLER.
⑥ REFLUX.
⑦ DISTILLATE.
⑧ PRESSURE REGULATOR.
⑨ HEATING COIL.
⑩ HEATER BODY.

Part of these distillations as described here have also been carried out while passing a current of air.

Typical distillation data of the type indicated above are shown as follows:

Weight of Bitterns for distillation 915 g.

Distillate		Residue	
First fraction	100 cm.^{3}	First Residue	85 g.
Second fraction	111 cm.^{3}	Second Residue	94·8 g.
Third fraction	110 cm.^{3}	Third Residue	239 g.
Fourth fraction	90·5 cm.^{3}		
Fifth fraction	60 cm.^{3}		
Total	461·5 cm.^{3}	Total	418·8 g.

Therefore Grand Total 880·3 g.

loss 34·7 g.

and percentage recovery of material 96·3 per cent.

In some cases, when distilling on a large scale for the recovery of large quantity of water, the very first distillate (cut fraction) was subjected to fractional distillation.

(*c*) *Fractional Distillation of Water after Separation from Bitterns*. Water, already obtained during the initial distillation for the recovery of large quantity of water from Bitterns as the starting material, was subjected to further [illegible]tions, and was fractionally distilled. Further enrichment of the heavy [illegible] was carried out by this fractional distillation.

Water separated from Bitterns after treatment as described in 3(*b*) was then subjected to fractional distillation in packed columns of different theoretical plates for investigations of further possible enrichment at normal temperature and pressure. Small-scale and large-scale fractionations have been carried out at different reflux ratios. All these fractional distillation operations were of batch distillation type. A typical distillation arrangement is represented in Fig. 3, and the typical data of such an operation are indicated below:

Packed Column height	= 680 mm.
Packed Column inner diameter	30 mm.
Packing material:	4 mm. single turn helical glass rings with a thin layer of 5 mm. porcelain Raschig rings on top.
Probable number of transfer units at 60 cm./sec.	54 H.E.T.P.
Reflux Ratio	17 : 1

Volume taken for fractional distillation = 2000 cm.^{3}
(from the first cut fraction of a large-scale distillation)
Total Time = 9 hours.
Temperature of Distillation = 97·7° C. at 682 ·5 mm. Hg.

Distillate

First Fraction = 435 cm.^{3}
Second Fraction = 760 cm.^{3}
Third Fraction = 305 cm.^{3}
Fourth Fraction = 485 cm.^{3}
(Residual)

Total = 1985 cm.^{3}
Therefore, loss = 15 cm.^{3}

The fractions, thus separated, were collected for investigations in their D_2O tent. Such samples which have been further enriched by fractional distillation then been subjected to electrolysis and catalytic exchange as conventional cess for further enrichment.[7]

(*d*) *D_2O–Content of Water from Bitterns, and of the Fractional Distillation ducts of this Water.*—The D_2O-content of water samples has been found out by s spectrometric analysis which has been carried out at Harwell.[8] Table III tains the D_2O-content of the water after separation from the Bitterns.

TABLE III

D_2O-Concentration of water distillates from Bitterns, obtained by large-scale distillation in Copper Still

Amount of Bitterns = 73 litres of 29·5° Bé at 25° C.
Total Distillate obtained = 43·150 litres.

	Volume cm.^{3}	Atom % D_2O	D_2O-content g.	% D_2O Distribution	% Volume Distribution	% Volume Σ
	20,080	0·0257	5·1606	57·42	46·3	46·3
	13,260	0·0165	2·1879	24·35	30·7	77·0
	9,360	0·0165	1·5444	17·19	21·7	98·7
	450	0·0205	0·0926	1·04	1·3	100·0
..	43,150		8·9855	100·0	100·0	

, average = $\frac{8\cdot9855}{43\cdot150}$ = 0·0208 mol. per cent. D_2O (atom per cent. D equivalent to mol. per cent. D_2O).

It can be seen from the following calculations, that the enrichment figure is found to be lower, as calculated from Rayleigh's equation at 40° C. If however, 50° C. is assumed to be the average solar evaporation temperature, instead of 40° C., the values are almost in complete agreement:

Rayleigh's equation:

$$\ln\frac{W}{W_0} = \frac{1}{\alpha - 1}\ln\frac{x(1-x_0)}{x_0(1-x)} + \ln\frac{1-x_0}{1-x}$$

Where

W_0	Original weight of water
W	Final weight of water of Bitterns.
x_0	Percentage of D_2O in sea-water.
x	Percentage of D_2O in Bitterns.
α	Relative volatility of heavy water with respect to light water (Ratio of vapour pressures[2])

At 40° C.

α = 0·892

W_0 = 99·23 kg. (*Ref.* Page 78)

W = 1·82 kg. (*Ref.* Page 78)

x_0 = 0·0145 mol. per cent. D_2O (normal abundance figure)

Therefore

x = 0·0224 mol. per cent. D_2O (as calculated from the above equation).

At 50° C.

α = 0·909

W_0, W, x_0 are same as before.

Therefore

x = 0·0208 mol. per cent. D_2O (as calculated from the above equation).

This value is in agreement with the average value as found in Table III.

While values of spectrometric measurements were used as correct values, investigations of our day-to-day work were carried out with the help of especially suitable gravimetric method which, however, was found useful only as a relative method, and did not yield absolutely correct figures. This method, at present, is undergoing further improvements.

In all fractional distillations of batch type it was found that contrary to our expectations, the first fractions always showed higher enrichment of D_2O, as ascertained by mass spectrometric analysis. Table IV contains the results of a carefully carried out fractional distillation of a part of fraction number I (*Ref.* Table III) of initial distillation.

TABLE IV

Enrichment of D_2O-Content in distillate *obtained from evaporation of Bitterns in Packed Column of* 680 *mm. height,* 30 *mm. internal diameter,* 4 *mm. single-turn helical glass rings as packing material*

Reflux ratio = 17 : 1. H.E.T.P. = 54. Volume of Feed = 2000 cm.^{3} (First Batch)

Fraction	Volume cm.^{3}	Atom % D_2O	D_2O-content g.	% D_2O Distribution	% Volume Distribution	% Volume Σ
1	435	0·0550	0·239	46·9	22·0	22·0
2	760	0·0162	0·123	24·1	38·3	60·3
3	305	0·0164	0·050	9·8	15·4	75·7
4 (Residual)	485	0·0202	0·098	19·2	24·3	100·0
TOTAL ..	1985		0·510	100·0	100·0	

Therefore, average = $\frac{0\cdot510}{1985}$ = 0·0257 mol. per cent. D_2O (atom percent. D equivalent to mol. per cent. D_2O).

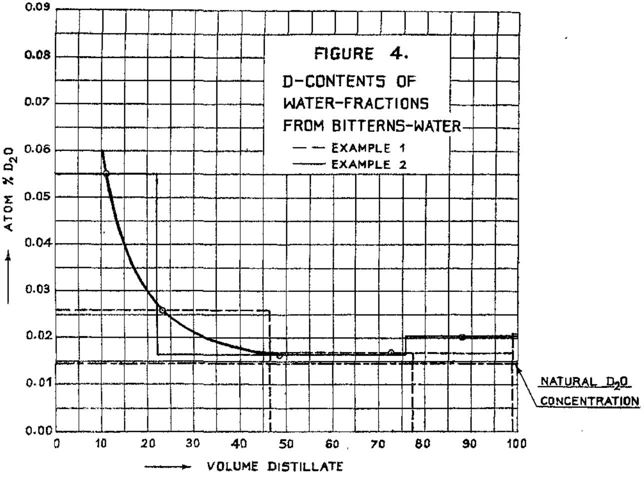

Fig. 4 contains the plot of the D_2O-content found in different fractions of a large-scale initial separation distillation of water from Bitterns during which different fractions were obtained (Example 1), and of a carefully carried out fractional distillation of a part of fraction Number 1 of the initial distillation (Example 2 as shown in Table IV).

From the values of the first fractions, as indicated in Tables III and IV, and represented in Fig. 4, it is obvious, that the D_2O-content will increase, the less is the quantity collected as the initial fraction. This phenomenon is under further investigation and cannot be explained properly at present. As, in the case of batch operation, the only difference between initial and final stages of the distillation consists in the presence of air at the initial stage, which, soon, is removed completely by the water vapours it might be possible that some kind of azeotropic mixture may exist between the components, heavy water or N_2 or O_2, which facilitates enrichment as long as this mixture is being maintained. The effect, however, of this phenomenon is very obvious from Table IV as with only 22 Vol. per cent. of the liquid, nearly half of the heavy water (46·9 per cent.) is being separated.

An attempt was made to explain the above results, expressed as relative volatility:

$$\alpha_{(H_2O)\,(D_2O)} = \frac{\gamma_{H_2O} \cdot P_{H_2O}}{\gamma_{D_2O} \cdot P_{D_2O}} . \tag{1}$$

where,

$\frac{P_{H_2O}}{P_{D_2O}}$ = Ratio of vapour pressures of the two components at a particular temperature.

γ_{H_2O}, γ_{D_2O} = are the activity coefficients.

At the point of azeotropism,

$$\alpha_{(H_2O)\,(D_2O)} = 1, \tag{2}$$

i.e.,

$$\frac{\gamma_{D_2O}}{\gamma_{H_2O}} = \frac{P_{H_2O}}{P_{D_2O}} . \tag{3}$$

Also,

$$\frac{\gamma_{D_2O}}{\gamma_{H_2O}} = \frac{y_{D_2O}}{y_{H_2O}} \cdot \frac{x_{H_2O}}{x_{D_2O}} \cdot \frac{P_{H_2O}}{P_{D_2O}} . \tag{4}$$

where, y terms represent composition in the vapour phase and x terms in the liquid phase, in mol. per cent.

Now, if

$\alpha_{(H_2O)\,(D_2O)} < 1$, then more of D_2O will come out in first fraction in comparison

For

$$\alpha_{(H_2O)\,(D_2O)} < 1,\ \frac{y_{D_2O}}{y_{H_2O}} \cdot \frac{x_{H_2O}}{x_{D_2O}} > 1 \qquad (5)$$

Calculations:

(i) For large-scale distillation:

$$x_{D_2O} = 0{\cdot}000208$$

$$x_{H_2O} = 0{\cdot}999792$$

For *first fraction* of fractional distillation,

$$y_{D_2O} = 0{\cdot}000550$$

$$y_{H_2O} = 0{\cdot}999450$$

Therefore,

$$\frac{y_{D_2O} \cdot x_{H_2O}}{y_{H_2O} \cdot x_{D_2O}} = \frac{0{\cdot}000550 \times 0{\cdot}999792}{0{\cdot}999450 \times 0{\cdot}000208} = 2{\cdot}645.$$

Hence,

$\alpha_{(H_2O)\,(D_2O)} < 1$, *i.e.*, D_2O should be more in this fraction in comparison.

(*ii*) For *Second fraction* of fractional distillation

$$y_{D_2O} = 0{\cdot}000162$$

$$y_{H_2O} = 0{\cdot}999838$$

Therefore,

$$\frac{y_{D_2O} \cdot x_{H_2O}}{y_{H_2O} \cdot x_{D_2O}} = \frac{0{\cdot}000162 \times 0{\cdot}999792}{0{\cdot}999838 \times 0{\cdot}000208} = 0{\cdot}779.$$

Hence,

$\alpha_{(H_2O)\,(D_2O)} \nless 1$, *i.e.*, D_2O should not be more in this fraction in comparison.

(iii) For *third fraction* of fractional distillation,

$$\frac{y_{D_2O} \cdot x_{H_2O}}{y_{H_2O} \cdot x_{D_2O}} = \frac{0{\cdot}000164 \times 0{\cdot}999792}{0{\cdot}999836 \times 0{\cdot}000208} = 0{\cdot}788.$$

Hence,

$\alpha_{(H_2O)\,(D_2O)} \nless 1$, *i.e.*, D_2O should not be more in this fraction in comparison.

(iv) For *residual fraction* of fractional distillation,

$$\frac{y_{D_2O} \cdot x_{H_2O}}{y_{H_2O} \cdot x_{D_2O}} = \frac{0{\cdot}000202 \times 0{\cdot}999792}{0{\cdot}999798 \times 0{\cdot}000208} = 0{\cdot}971.$$

Hence

$\alpha_{(H_2O)\,(D_2O)} \nless 1$, *i.e.*, D_2O should not be more in this fraction in comparison.

With reference to Table IV, the value of D_2O-content in the residual fraction of the first batch is 0·0202 mol. per cent D_2O. Residual fractions of other batches also yielded similar values.

At this stage, it is worthwhile pointing out that, similar enrichment of heavy water, as in Bitterns, may be found in such waters of lakes which dry up considerably, as in the water of the Dead Sea, in hot springs, in volcanic waters, and even in residual liquors of some processes, e.g., in spent liquors from [illegible] salt mines. All these potential sources, therefore, require more close investigations for heavy water content.

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